Molecular Foundry
Research Highlight
LBNL Materials Sciences Division

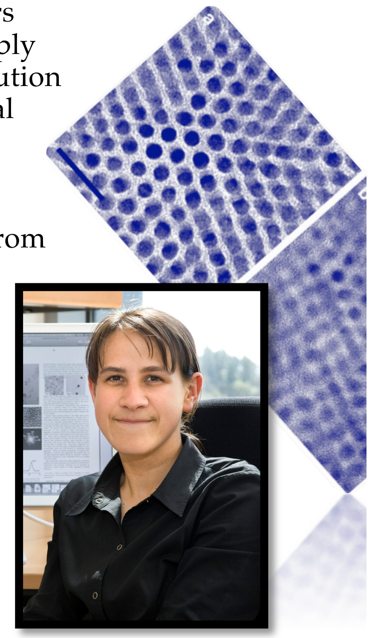
U.S. Department of Energy
Materials Sciences and Engineering Division

Mix–and Match Inorganic Nanocomposites by Solution Processing

A team of researchers led by Delia Milliron of the Molecular Foundry, Materials Sciences Division, LBNL has developed a new approach for the synthesis of inorganic nanocomposites. This solution-based technique is materials-general so that it could be applicable to a wide range of materials for use in a variety of applications, including battery electrodes, thermoelectrics, photovoltaics, and electronic data storage.

Nanocomposites – multi-component materials in which the components are intermixed on the nanoscale – can exhibit qualitatively different properties compared either to homogeneous materials or composites with larger scale components. Although this is understood to be the result of the extremely high density of interfaces at the nanoscale, existing methods for nanocomposite synthesis, such as thermal- or reaction-induced microphase separation or growth of nanoparticles within a porous matrix offer limited opportunities for the controlled variation of the component materials and morphology.

Milliron and postdoc Ravisubhash Tangirala have designed a new synthesis method with the goal of controlling the morphology of a specific type of nanocomposite – ordered particle assemblies in a solid matrix – over a wide range of compositions. The process involves first making the individual components – colloidal nanoparticles and soluble precursors to the matrix phase – by solution-phase chemistry. The colloidal nanoparticle synthesis routes offer considerable flexibility in controlled synthesis of nano- rods, spheres, tetrapods etc. These can then be used to form a range of assemblies including ordered superlattices, binary assemblies of two different sizes and/or types of nanoparticles and vertically oriented arrays of nanorods. The key step to forming an inorganic nanocomposite from any of these nanoparticle assemblies, involves replacing the organic ligands (which initially coat the surface of the nanoparticles and fill the interparticle spaces), with chalcogenidometallate clusters (ChaMs). This is done by simply soaking the assembly in a solution containing the ChaM. Thermal annealing crosslinks the ChaMs, forming thermally a stable nanocomposite whose components can be selected from a wide range of nanoscale building blocks.



> "This new process for fabricating inorganic nanocomposites gives us unprecedented ability to tune composition and control morphology."
>
> D. Milliron

The team demonstrated the generality of the method by creating nanocomposites of more than 20 different compositions, starting from assemblies of spherical or rod-shaped nanoparticles. They also showed that the structural ordering in the nanoparticle assemblies persists throughout the process.

The new method should enhance flexibility for exploration and optimization of materials properties, and should enable development of materials for a wide range of applications. For example, nanocomposites of lead chalcogenide nanoparticles (PbSe or PbTe) in a complementary matrix material such as antimony selenide (Sb_2Se_3) have potential for thermoelectric (thermal to electrical) energy conversion. Additionally, vertical arrays of cadmium sulfide (CdS) nanorods in a copper sulfide (Cu_2S) matrix are intriguing possibilities for photovoltaic cells. As a final example, composites containing nanoparticles with high ionic and electronic conductivity, such as silver sulfide or telluride (Ag_2S, Ag_2Te), in glassy germanium sulfide (GeS_2) matrices are model systems for understanding transport processes in nanostructured battery electrodes and data storage devices.

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R Tangirala, JL Baker, AP Alivisatos, DJ Milliron, "Modular inorganic nanocomposites by conversion of nanocrystal superlattices," Angew. Chem. Int. Ed. 49 (2010), 2878.

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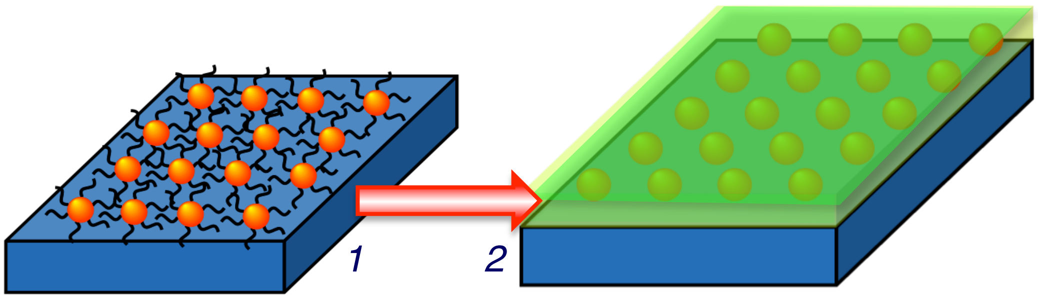
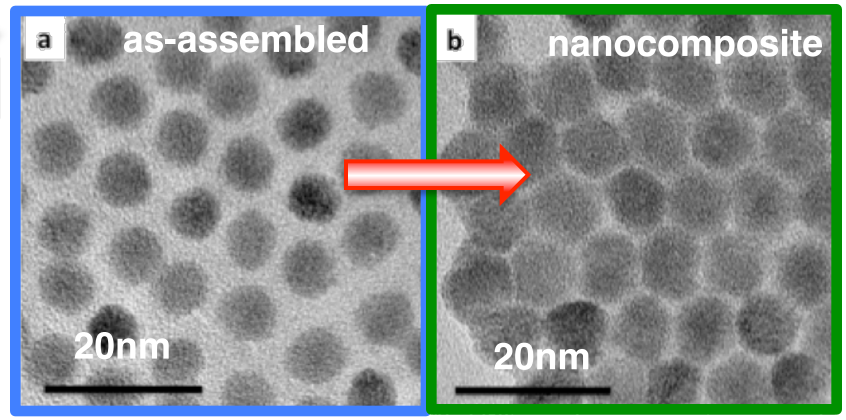
Spherical PbSe array



***Two step nanocomposite fabrication process**:*
(1) Ordered arrays of nanocrystals (top left) and nanorods (below left) coated in organic ligands synthesized on a surface. (2)The material is then soaked in a solution containing chalcogenidometallate clusters (ChaMs), which replace the organic ligands. Thermal annealing crosslinks the ChaMs, forming nanocomposite (2).



***Transmission electron microscopy (TEM) of nanocomposites**:*
Panel a (top, bottom left) shows the original nanoparticle superlattices. Panel b (top, bottom right) shows the inorganic nanocomposites. Nanoparticle ordering is maintained and the spacing between them decreases upon composite formation

CdS Nanorod array